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(54) Title: APPARATUS AND METHOD FOR FLUORINE PRODUCTION

(57) Abstract: Apparatus and a method for the generation of fluorine by the electrolysis of hydrogen fluoride are described. The apparatus comprises: a plurality of individual fluorine generating cassettes; said individual fluorine generating cassettes being opera-bly connected to a fluorine gas distribution system for the remote use and consumption of said fluorine gas; said fluorine generating cassettes being individually isolatable from said gas distribution system and removable from the apparatus for remote maintenance.

APPARATUS AND METHOD FOR FLUORINE PRODUCTION

5 The present invention relates to an apparatus and a method of using the apparatus for the production of fluorine.

Semiconductor devices, for example, are generally produced in vacuum process chambers by the chemical vapour deposition (CVD) of a plurality of layers of silicon for example. The constituent layers of material are also etched to provide a desired pattern on the device during its manufacture. Such etching in a vacuum 10 chamber results in some of the substrate material being etched, e.g. silicon, silicon oxide, silicon nitride, for example, being deposited on the process chamber surfaces over time. Most of the unused chemical reagents and by-products of the deposition or etching process are exhausted from the chamber at each process step, however, some of these essentially unwanted reagents and by-products are inevitably deposited on the process chamber 15 walls and surfaces and become potential contaminants. For example, it is possible for some of these deposited 20 materials to fall from the chamber walls and become incorporated in the devices themselves which would render them as scrap. Such unwanted deposits and residues must be periodically cleaned from the process chamber surfaces 25 before building up to undesirable and potentially harmful 30 levels.

Although semiconductor devices have been specifically referred to above, CVD is a very widely employed technique for the production of many types of electronic

devices. For example, CVD is used in the production of thin film transistors (TFT) flat panel displays by depositing films of material on large substrates such as glass panels, for example, in the production of liquid 5 crystal displays (LCD).

Conventionally, the cleaning of undesired materials from the surfaces of CVD process chambers was accomplished by use of cleaning gases such as nitrogen trifluoride, 10 hexafluoroethane and sulphur hexafluoride. Whilst these gases work well in removing contaminants from process chambers they have the disadvantage of contributing to global warming if released into the earth's atmosphere. These gases, in use, are decomposed by plasma means to 15 release atomic fluorine in the process chamber and which is the active cleaning constituent.

More recently it has been established that instead of the conventional gas compounds referred to above, molecular 20 fluorine gas may be used either directly or as atomic fluorine, after treating molecular fluorine in a plasma chamber, for CVD process chamber cleaning. Molecular fluorine has the added advantage that it does not contribute to global warming. EP-A-1 138 802 describes 25 the use of molecular fluorine for the removal of contaminant materials from CVD chambers.

However, whilst EP-A-1 138 802 discussed above makes it clear that molecular fluorine in itself or treated to 30 produce atomic fluorine is efficacious in cleaning CVD chambers, there is no hint as to how such gaseous fluorine may be generated to supply a commercial CVD plant.

The electronic devices manufacturing industry, however, is not well equipped to either maintain or deal with the conventional chemical plant installations which would be required to generate fluorine in the quantities necessary

5 for the cleaning of the number of CVD chambers which exist in a typical modern plant for the manufacture of electronic devices. The industry demands reliable, easily expandable on-site production and delivery of a high-purity fluorine gas stream. It is desirable that

10 maintenance and expansion of a fluorine generating plant be carried out quickly and simply with minimal or no chemical hazard and importantly, no loss of production during such maintenance or expansion. The aspect of expansion is important as some users will require that

15 fluorine generating capacity be increased as the required manufacturing capacity of electronic devices increases due to increased numbers of CVD chambers.

The use of compressed fluorine in cylinders for large

20 scale CVD applications is not practical due to safety concerns and the fact that the maximum quantity of fluorine stored at 28 bar gauge is only 1.4kg in a typical 50 litre cylinder. Thus, compressed fluorine in the quantities required at a normal commercial plant

25 represent an unacceptable environmental and safety hazard as the reactivity of fluorine increases greatly when compressed. Furthermore, the cost of providing large quantities of fluorine in such a manner would be prohibitive.

30 On-site generation of fluorine currently exists in some industries, however, the fluorine generating apparatus has been designed to suit chemical industry standards relating to fluorine generation and requires significant

35 on-site maintenance and frequent operator intervention

and often involves handling or sampling of chemicals such as the electrolyte from which the fluorine gas is produced. This procedure is common in the chemical industry where the expectation is that personnel will 5 wear appropriate protective clothing and use breathing apparatus, for example, to protect themselves from hazardous fluorine gas liberated to atmosphere when cell connections are broken or cells opened. However, this approach is not acceptable in the electronics industry 10 where the expectation is that personnel will not need to rely on protective clothing and the like and that any hazardous gases will be contained at all times and not liberated to atmosphere under any circumstances.

15 In the absence of a particular process benefit resulting from the use of molecular fluorine for CVD tool cleaning it has been expressed that a cost saving of at least 30% would be required for the industry to change from the existing methods and cleaning chemicals. Thus, it was 20 originally considered that each CVD process tool might be coupled to a conventional fluorine generating cell. This approach has obvious apparent benefits in that the output of the fluorine cell may be matched to the fluorine requirements of the particular tool which it supplies.

25 Such an approach would also minimise fluorine process piping. A further apparent advantage is that failure of one fluorine generator would not result in a plant-wide shutdown, only a shutdown of one CVD tool. However, in reality, the superficial attractions of one fluorine 30 generator per CVD tool are outweighed by the practical and economic disadvantages of such an approach. Each fluorine generator would have to have the same process modules and would thus necessitate unnecessary and costly duplication of components and services, including: 35 anhydrous hydrogen fluoride supply, downstream

purification of the fluorine gas, gas compression and storage and generator effluent abatement. Thus, this proliferation would result in the distribution of a relatively hazardous chemical process, including large 5 hydrogen fluoride inventories and fluorine gas storage across an entire production plant. As a consequence of this, all fluorine generator operation and maintenance activities would be similarly distributed which would have adverse implications for plant safety.

10

Additionally, fluorine gas quality is of paramount importance in CVD cleaning applications and gas quality control is much more difficult as continuous on-line analysis is prohibitively expensive when several 15 installations would be required and periodic fluorine gas sampling from a plurality of installations has many practical and safety drawbacks.

In contrast to the one fluorine generator per tool 20 approach described above, the single, large conventional generator with separate feeds to a plurality of CVD tools has the overwhelming disadvantage that failure or shutdown of the generator for repair or maintenance results in the entire production process being halted for 25 however long the generator is out of commission.

A first aspect of the present invention relates to 30 apparatus for the generation of fluorine by the electrolysis of hydrogen fluoride, the apparatus comprising: a plurality of individual fluorine generating units; said individual fluorine generating unit being operably connected to a fluorine gas distribution system for the remote use and consumption of said fluorine gas; said fluorine generating units being individually

isolatable from said gas distribution system and removable from the apparatus for remote maintenance.

5 In the above, the word "maintenance" is intended to cover any reason whatsoever for the removal of the individual fluorine generating unit from the apparatus. In the present invention the word "maintenance" may, for example, include routine maintenance, servicing or repair of that cell. It is further intended that such a cell
10 requiring maintenance be removed from the apparatus and taken to a remote site away from the plant where the fluorine is being consumed such that there is no inconvenience, contamination or safety hazard to the production plant or personnel.

15 In this specification the apparatus is a "packaged" fluorine generating apparatus. The term "packaged" is intended to mean a plant which is built and assembled at a fluorine plant supplier company, for example, tested to
20 ensure efficient operation of the apparatus, closed down, sealed and then shipped as a self-contained plant to a customer site, for example, for use of the fluorine in the customer's processing. Generally, the apparatus may be totally self contained; apart from customer provided
25 services such as electricity, water, compressed air or nitrogen supplies, for example, to render the apparatus operative; in a container shippable by land or sea and that container being the container in which the apparatus will reside and operate at the customer's site.

30 Packaged fluorine generating plant or apparatus may be generally categorised as apparatus intended to produce in total from 0 to 2.7 kg of F₂ per hour. There exist conventional large scale fluorine generating plants in
35 the chemical industry which are capable of producing

several thousand tonnes of fluorine per year, where each cell will typically generate not less than 4 kg of fluorine per hour, these plants being able to have individual cells removed by personnel wearing and using appropriate safety equipment, they are built in-situ for a plurality of cells and associated equipment brought to site of operation and assembled. Such plants are used, for example, in the nuclear industry for the production of nuclear fuel precursors such as uranium hexafluoride, for example. Such plants are quite different and distinct from the "packaged", transportable as a unit fluorine generating apparatus forming the subject matter of the present invention. In the present invention the apparatus may be contained, for example, within a container having overall dimensions substantially not more than a standard ISO container or less as explained in greater detail below.

In this specification, the apparatus comprises a plurality of self-contained fluorine generating units. The units may be constituted by a single cell insofar as that unit has effectively one cathode and one anode. Alternatively, the unit may comprise a group of cells insofar as there may be more than one cathode and anode in that unit. Thus, the apparatus according to the present invention comprises a plurality of fluorine generating units which are isolatable one from another and from the apparatus as a whole and each unit is individually removable from the apparatus without interrupting the supply of fluorine from the apparatus as a whole. In the interests of ease of description, an individual fluorine generating unit will henceforth be termed a "fluorine cassette". Similarly, other facilities in the fluorine producing apparatus such as fluorine purification units and fluorine compression and storage

units are also termed "cassettes", e.g. "purification cassette" and "compression and storage cassette". The term "cassette" is intended to convey the meaning of a self contained package having the described feature or

5 facility which may be easily removed from the apparatus for maintenance or repair and be replaced by an identical package without danger to people or detriment to the smooth production of fluorine.

10 It is common terminology in the fluorine generating industry to refer to a fluorine "cell" as one metal container vessel but which vessel may possess a plurality of anodes therein (the container itself normally constitutes the cathode). Prior art fluorine cells may

15 typically have up to 36 separate anodes. Thus, in the present invention, each fluorine cell or cassette may have, for example, 6, 12 or 24 anodes depending upon the customer's fluorine requirements.

20 It is also further intended that the removed fluorine cassette be replaced with another substantially identical fluorine cassette such that the fluorine generating capacity of the apparatus is not significantly impaired.

25 The apparatus according to the present invention provides a self contained fluorine generation system which has sufficient fluorine generating capacity for the plant, for example as a cleaning gas for CVD chambers or tools, to which it is connected such that the total fluorine

30 demand may be met by less than the total number of individual fluorine cassettes in the apparatus. Thus, if one fluorine cassette, for example, requires repair or maintenance or servicing then the apparatus may continue to generate the total fluorine requirement without shut-

35 down of the fluorine generating apparatus according to

the present invention or other interruption. As noted above, the removed fluorine cassette may be immediately replaced with a substantially identical (in important material and dimensional respects) fluorine cassette so

5 that total potential fluorine generating capacity is not impaired at all. For example, for apparatus having three fluorine generating cassettes, the normal average output of the three cassettes will be less than 66% of peak output of each cassette at peak demand. Therefore, if one
10 cassette needs to be removed for any reason, the two remaining cassettes will be able to meet the total peak fluorine demand of the application which the plant is supplying.

15 Thus, a single point failure of a fluorine cassette of the apparatus of the present invention does not result in shut-down of the apparatus as a whole nor a reduction in the ability to supply the peak demand of fluorine.

20 As noted above, fluorine generating cells have traditionally been maintained, serviced or repaired in-situ which has necessitated closing down the cell and dismantling it in-situ which, because of the extremely hazardous nature of fluorine gas and the electrolytes
25 employed, has meant that all but essential personnel, suitably attired, must be evacuated from the area whilst the work is undertaken. Usually the down-time has been several days to complete the work. This has meant disruption and lost production time in the plant which is
30 fed by the fluorine apparatus.

With the apparatus of the present invention, it is intended that the fluorine cassette requiring work is isolated electrically and by valve means insofar as the
35 fluorine gas aspect is concerned, removed from the

apparatus and transported, by truck for example, to a remote site where the required work is undertaken. However, a replacement fluorine cassette, held as a spare in store on-site, may be immediately installed in the 5 apparatus. Thus, there are no time constraints on the time required for the removed cell to be brought operational again; the cell may be worked on at a site which is properly equipped for such work; no hazard is produced in respect of those people working at the plant 10 from where the fluorine cassette was removed; and, there is no lost production time at the plant.

The apparatus according to the present invention may be relatively small in terms of overall size. It may, for 15 example, as noted hereinabove, approximate the size of a standard ISO container which are used internationally for shipping and transportation of many types of goods. Such containers have an overall size of about 2.44m wide X 2.44m high X 6.5m long (or about 8' wide X 8' high X 20' 20 long in Imperial measurements). Thus, the fluorine generating apparatus of the present invention may have a small footprint and be easily situated in a convenient location within a customer's production plant.

25 The apparatus of the present invention comprises an integrated, self-contained fluorine generating plant which may be shipped as a unit by land or sea. The apparatus according to the present invention when based on an ISO type container may comprise up to three 30 fluorine cassettes, at least one fluorine purification cassette and at least one fluorine compression and storage/buffer cassette.

One embodiment of the present invention comprises a 35 fluorine generating apparatus having three fluorine

5 cassettes, two fluorine purification cassettes, a fluorine compression and storage cassette and other associated equipment all enclosed within the outer dimensions of a standard ISO container. However, there is
10 another aspect of shipping and that is the shipping of spare or replacement fluorine cassettes; a standard ISO container may accommodate up to eight fluorine cassettes based on a width of approximately 0.74m, however, this is given as an example only as the individual fluorine
15 cassettes may be constructed in a range of individual sizes. The cassettes of the apparatus of the present invention are self-contained shipping packages by virtue of their outer enclosure which is completely panelled making the cassette a sealed unit and needing no further packaging or protection for shipping.

Although the fluorine cassette for a particular apparatus according to the present invention may be formed to a particular set of outer dimensions and have services connections and fluorine outlets and hydrogen outlets and the like in predetermined positions so as to ensure interchangability, the actual fluorine cell within the fluorine cassette may be varied to suit the fluorine demand of a customer. For example, the fluorine cell may initially have a fluorine generating capacity of 0 to 385 g/hr and, as demand increases, may be changed for a fluorine cell having an output capability of 0 to 700 or 0 to 1400 g/hr, for example. Thus, the apparatus according to the present invention may be upgraded as fluorine need increases.

The fluorine cassettes may be installed within an overall apparatus enclosure which may house common services for all the fluorine cassettes within that apparatus enclosure. Such common services may include fluid piping,

electrical cable trunking and electrical/instrument wiring harnesses.

Hazardous fluid services to the fluorine cassettes are 5 provided with isolation valves. Preferably, the hazardous fluid services to the cassettes are provided by double isolation valves which have a vacuum connection in between. Thus, the two isolation valves may be closed and vacuum applied to remove hazardous contents before 10 breaking the connection between the fluorine cassette and the associated piping prior to removal of the fluorine cassette from the apparatus. The vacuum extraction system for removing hazardous materials is preferably connected to a scrubbing system for removing and neutralising 15 harmful materials.

Non-hazardous fluid services may be provided by means of quick-connect couplings, for example.

20 Once the fluorine cassette is disconnected from the apparatus it is completely sealed from the ambient environment and constitutes no danger to personnel. Similarly, a new replacement fluorine cassette is also harmless until it is connected into the apparatus and the 25 isolation valves opened to permit flow of hazardous fluids.

Spare fluorine cassettes may be stored on-site to enable 30 quick replacement. Similarly, removed cassettes may be safely stored on site until they can be removed to a remote repair or servicing facility off-site, for example.

The fluorine cassettes may be provided with means to 35 facilitate moving the cassette into and out of the

apparatus enclosure. Suitable means may comprise wheels, for example.

In a preferred embodiment of the present invention the 5 fluorine cassette is itself be provided with a self-contained enclosure around the fluorine generating cell or cells such that any leakage of fluorine gas for example is contained within the enclosure. More 10 preferably, the cassette enclosure may be connected to a vacuum extraction system which is provided with scrubbing means to remove harmful chemicals.

In the apparatus of the present invention each cassette has its own enclosure provided by a strong metal frame 15 and panelling. When installed in the apparatus the enclosure is connected to extraction and scrubbing means to deal with any potential leaks, and therefore, provides a sealed protective enclosure. When the cassette is removed from the apparatus, the enclosure provides the 20 dual advantage of constituting protection for the cassette during shipping without further packaging and protection for people handling the cassette.

In a preferred embodiment of the apparatus according to 25 the present invention there is also provided at least one, preferably two fluorine purification cassettes through which the output of the fluorine cassettes is passed so as to remove unwanted particulate material or undesirable gaseous contaminants therefrom before it 30 reaches any process equipment for which it is destined. The purpose of having two such cassettes is to allow for one cassette needing repair or replacement during fluorine production. Such unwanted material may include 35 hydrogen fluoride, for example, carried over from the electrolyte in the fluorine stream and which may be

passed through a sodium fluoride trap, for example. Carbon tetrafluoride formed by reaction of fluorine with the carbon anodes may be removed by an appropriate known adsorption system.

5

The fluorine purification cassette may also be isolatable and easily removed from the apparatus for repair and servicing in a similar manner to the fluorine cassettes. Thus, such isolation may be accomplished preferably by 10 double isolation valves with an intervening vacuum extraction facility as with the fluorine cassettes.

In a further preferred feature of the apparatus according to the present invention, there may also be provided a 15 fluorine buffer cassette connected in the fluorine line downstream of the fluorine purification cassette. In effect, the buffer cassette collects purified fluorine being generated and holds it in tanks so as to provide a fluorine reservoir to smooth out fluctuations in supply 20 and provide fluorine at a constant pressure.

The apparatus according to the present invention may all be housed within a main enclosure framework which is provided with suitable panelling so as to effectively 25 render the enclosure sealed to the outside ambient atmosphere. Further preferably, the main enclosure is provided with evacuation means so that any leakage is removed and does not contaminate the surrounding area. The evacuation system may be connected to suitable 30 scrubbing means for the removal and safe disposal of any harmful substances.

The main enclosure may also preferably be provided with all of the necessary electrical power supply and 35 electrical control systems in known manner so as to

effect electrolysis of the hydrogen fluoride electrolyte to generate fluorine.

According to a preferred embodiment of the apparatus
5 according to the present invention the framework of the fluorine cassette may be utilised as the cathode connection of the fluorine cell or cells within the cassette thus, the mere installation of the cassette within the main enclosure effects the necessary cathode
10 connection to the electrolytic cell or cells within the cassette.

Preferably, the apparatus according to the present invention is further provided with purging means to
15 remove potentially reactive fluids such as moisture, for example, from piping before fluorine is introduced. Such purging means may comprise valve means connected to apparatus piping for the introduction of nitrogen, for example, into the piping so as to purge oxygen, for
20 example, from the piping.

In an alternative embodiment of the apparatus according to the present invention, each individual fluorine cassette may be provided with the necessary facilities so
25 as to enable the apparatus to continue to function even if some "centralised" apparatus services should fail. In this alternative embodiment, the self-contained cassette enclosure may also be provided with a D.C. power supply unit for electrolysis, fluorine purification and
30 compressor means and a fluorine storage tank/buffer facility. The cassettes are of relatively large volume and the fluorine generating unit is housed in the lower portion of the cassette enclosure leaving sufficient room to accommodate the additional facilities. Connections to
35 the storage tank/buffer facility may also be by double

isolation valves. In this alternative embodiment, disconnection of the cassette from the apparatus enclosure would be from the output of the fluorine tank/buffer unit as the fluorine cell per se, 5 purification and compression facilities are upstream therefrom.

According to a second aspect of the present invention, there is provided a method for the operation and 10 maintenance of apparatus for producing fluorine by the electrolysis of hydrogen fluoride, the method comprising the steps of: providing a plurality of fluorine generating units operably connected to a fluorine gas distribution system for the remote use and consumption of 15 said fluorine; providing means for isolating an individual fluorine generating unit from said fluorine gas distribution system and from each other; and providing means for the disconnection and removal of said isolated fluorine generating unit from said apparatus 20 without interruption of supply of fluorine from remaining fluorine generating units.

The same definition relating to fluorine generating units is utilised in the method according to the present 25 invention as in the apparatus according to the first aspect of the invention.

In order that the present invention may be more fully understood, examples will now be described by way of 30 illustration only with reference to the accompanying drawings, of which:

Figure 1 shows a schematic cross sectional representation of a prior art fluorine producing cell;

Figure 2A shows a front elevation (without panelling) of a first embodiment of apparatus according to the present invention;

5 Figure 2B shows an end elevation of the apparatus of Figure 2A;

Figure 3 shows a side elevation of a fluorine cassette of Figure 2 without enclosure panelling;

10

Figure 4 shows a front elevation of the fluorine cassette of Figure 3 without enclosure panelling;

15

Figure 5 shows a side elevation of a fluorine purification unit without panelling of the apparatus of Figure 2;

Figure 6 shows a front elevation of the purification unit of Figure 5;

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Figure 7 shows a side elevation of a buffer unit without enclosure panelling of the apparatus of Figure 2;

25

Figure 8 shows a front elevation of the buffer unit of Figure 7; and

30

Figure 9 which shows a perspective view of a second embodiment of apparatus according to the present invention but with main and other enclosure panelling removed in the interests of clarity.

35

Referring now to Figure 1 which is intended only to explain the basic principles of the production of fluorine by electrolysis. A fluorine generating cell is shown schematically in section at 10. The cell comprises

a containment vessel 12 which may or may not also constitute the cathode of the cell; in this case a separate cathode is shown at 14. The top 16 of the vessel 12 is closed save for outlets 18, 20 having valve means 5 for fluorine and hydrogen, respectively. The vessel 12 contains an electrolyte 22 of hydrogen fluoride in a molten potassium fluoride salt. A separating skirt 24 depends from the vessel top wall 16 and its lower end 30 extends below the surface 32 of the electrolyte 10 effectively dividing the volume above the electrolyte surface into two separate chambers 34, 36 for hydrogen and fluorine, respectively. An anode 38 generally of high-density isotropic carbon extends into the electrolyte 22 and generally extends below the lowermost 15 extent of the skirt 24 although this may not always be the case. The vessel 12 is generally provided with means (not shown) to heat and melt the electrolyte as it is solid at room temperature. Generally, the electrolyte is maintained in the range from 80 to 100°C by the heating 20 means when the cell is quiescent. During electrolysis heat is generated and is generally necessary to cool the electrolyte by suitable cooling means. Any suitable heating means may be used and, for example, may comprise tube heaters extending into the vessel and passing 25 through the electrolyte, an electrically heated blanket around the vessel or a steam jacket around the vessel. A suitable power supply 40 is provided to effect electrolysis of the electrolyte. Generally, the voltage is relatively low at about 6 to 9 volts but the current 30 is high at about 500 to 2400 amps depending upon the number of anodes in the cassette.

The electrolysis reaction is:



The amount of fluorine generated is in direct proportion to the applied current. The gases, fluorine and hydrogen, rise substantially vertically from the anode and cathode 5 surfaces into their respective compartments above the electrolyte surface 32. The electrolyte temperature is regulated as noted above and the composition and level is controlled by the addition of anhydrous hydrogen fluoride.

10

Turning now to Figures 2 to 8 and where the same features are denoted by common reference numerals. Apparatus according to a first embodiment of the present invention is shown at 100; the apparatus comprises a main enclosure 15 framework 102 which has removable panelling (not shown) to form a main sealed enclosure 104 in use and which sealed enclosure is connected to a vacuum extraction system (not shown) via a manifold 124 which in turn is connected to a scrubbing system (not shown) to neutralise 20 harmful chemicals. Within the main enclosure 102, 104 are housed three fluorine cassettes 106, 108, 110 which are all substantially identical in the sense that each may be substituted for another and have the same positioning of connection fittings such as isolation valves, pipes, pipe 25 fittings, electrical services and the like, for example. The fluorine cassettes are connected to a fluorine gas manifold 114 for off-take of fluorine process gas as it is produced by the fluorine cassettes via a fluorine gas standpipe 116 connected to the fluorine compartments of 30 the electrolytic cells in the cassette (see Fig.1 above and also below for more detailed description of the fluorine cassette). The standpipe 116 is connected to the manifold 114 via double isolation valves 118, 120, the intervening space between which is connected to the 35 vacuum extraction fluorine manifold 124 which in turn is

connected to the scrubbing system (not shown) for neutralising any harmful gases. The hydrogen produced during electrolysis is piped away via a standpipe 130 on each cassette, the standpipes being connected via flanged 5 joints 132 to a hydrogen gas manifold 134 which conducts the hydrogen away for either treatment or burning-off as appropriate. All of the pipe work through which fluorine flows is connected via suitable valve means (not shown) to a source of a purging gas (not shown) such as 10 nitrogen, for example, to permit purging of oxygen and/or moisture from the pipe work prior to the introduction of fluorine.

Each individual fluorine cassette 106, 108, 110 comprises 15 a cassette enclosure frame 140 which is able to be split horizontally into two parts: a lower part 142 which houses the fluorine generating cells 144; and, an upper part 146 which houses power supplies for electrolysis and the like. Splitting of the cassette enclosure permits 20 easy access to the fluorine generating cells after removal of the cassette from the main enclosure 102, 104. To aid mobility, the fluorine cassette is provided with wheels 148 to facilitate removal from the main enclosure 102, 104. The cassette shown in Figs 3 and 4 has one cell 25 producing fluorine but, however, the cell may contain 6, 12 or 24 anodes depending upon required fluorine generating capacity as explained hereinabove. The total output of fluorine in each cassette is conducted internally to the single fluorine off-take pipe 116 30 having the double isolation valves 118, 120. Similarly, all hydrogen generated during electrolysis is conducted to the single off-take standpipe 130. The fluorine generating cells 144 have a common containment vessel 150 fabricated from steel and forms the cell cathode and 35 which is welded to the lower part 142 of the enclosure

frame 140. Thus, the enclosure frame forms the cathode connection for the whole cassette. Each cassette may have its own D.C. power supply 152 and control system 154, however, the power supply and control system for all 5 cassettes may be centralised in the main enclosure 104. The upper part 160 of the main enclosure 102, 104 houses busbars and main power supplies (not shown) and the like to which each of the fluorine cassettes are connected on being installed into the main enclosure by means of plug-10 in electrical connectors (not shown) to a junction box 158.

As noted above the enclosure frame may form the cathode connection of the apparatus of the present invention. 15 Since the frame is the cathode it also carries the current which may be up to about 2400 amps with a 24 anode cassette. Thus, the frame is made of substantial section material in order to prevent undesirably high temperatures being reached due to resistance heating. The 20 cathode connection is made at 0 volts relative to earth whilst the anode connection is at 6 to 9 volts. Use of the enclosure frame as the cathode connection and current carrier enables the apparatus to be more economically made with a strong frame due to thicker section materials 25 and without unnecessary extra copper cabling to make the cathode conductors. Since the frame is a 0 volts relative to earth, the apparatus is electrically very safe.

The total fluorine output of the fluorine cassettes 106, 30 108, 110 is connected to a fluorine purification cassette 170 through which the fluorine is passed to remove particulate material such as hydrogen fluoride or other electrolyte constituents which have been carried over by the fluorine stream and contaminants formed during 35 electrolysis. The purification cassette is shown in more

detail in Figures 5 and 6. The purification cassette comprises a container 172 housing chemical traps and filters (not shown) for removing unwanted material from the fluorine stream in known manner. The purification cassette 170 has an enclosure framework 174 enclosing the container 172 and, in similar manner to the fluorine cassettes has a double isolation valve 178, 180 to permit installation in and removal of the purification cassette from the apparatus when required. The unit is provided with wheels 180 to aid moving.

The purified fluorine gas is passed from the cassette 170 to a fluorine compression cassette 190 shown in Figures 7 and 8. The compression cassette comprises, in this example, three holding tanks 192 having a total capacity of 650 litres and able to safely withstand 5 Bar pressure of fluorine although such pressures are not generally employed with fluorine in the interests of safety. The output of purified fluorine from the purification cassette 170 is fed to the compression cassette pump 194 and via a pressure controller 196 to the holding tanks 192. The compression cassette 190 holds a reserve of fluorine such that if for any reason the apparatus had to be closed down in respect of fluorine production for a period of time, for example, to change the purification cassette 170, then there would be a reserve of fluorine to continue with the process requirements until fluorine production can be resumed. The compression cassette also smoothes out fluctuations in fluorine production so that fluorine may be supplied to the process plant at a constant pressure, for example. In similar manner to the fluorine cassette and the purification cassette, the compression cassette has an enclosure frame 200 and wheels 202. The compression cassette is connected to the fluorine manifold 114 again by double isolation valves

(not shown) as with the fluorine cassette and the purification cassette. The fluorine output is via a second pressure controller 198 to the fluorine manifold 114 and then to the process plant where the fluorine is
5 to be used.

As may be seen from Figures 2A, 2B, 3 and 4 the fluorine cassette 106, for example, may be installed in and removed from the main enclosure 102, 104 without need to
10 interfere with the two other cassettes 108, 110 which may continue to provide fluorine for the required processes operated externally to the apparatus. The fluorine generating capacity of the apparatus 100 is calculated such that the total process requirements of the plant
15 being served may be met, for example, by any two of the three cassettes of the apparatus described thus allowing one cassette to be redundant or removed and replaced as required.

20 In the example described above the apparatus 100 approximates less than the size of an ISO container in terms of length, and therefore, may be easily transported by land or sea. It is further possible to provide the apparatus as described above but somewhat larger but
25 still within the footprint of a standard ISO container and having empty spaces therein so as to accommodate additional fluorine cassettes for example to provide expansion of fluorine generating capacity as need arises. The empty spaces may be provided with the necessary
30 valves and pipe connection to the manifolds etc so that an additional fluorine cassette may merely be connected into the system as with the existing cassettes.

The main enclosure frame 102 is provided with removable
35 panelling so as to effect a substantially sealed

enclosure, in use, to the egress of fluorine, for example. The enclosure is connected to the site extraction and scrubbing system to neutralise harmful chemicals. Furthermore, each fluorine cassette, 5 purification cassette and compression cassette is similarly equipped, in use, with panelling on the frames 140, 174 and 200 so as to form substantially sealed sub-enclosures within the main enclosure 102, 104, the sub-enclosures also being connected to the site extraction 10 and scrubbing system.

Figure 9 shows a single perspective view of a fluorine generating plant 300 according to a second embodiment of the present invention. In terms of the capacity and 15 capability to produce, process, control and store fluorine the apparatus of Figure 9 is similar to that described with reference to Figures 2 to 8 of the first embodiment. The apparatus 300 again has a main enclosure framework 302 which is provided with panelling (not 20 shown) to form a substantially sealed enclosure. Three fluorine cassettes 304, 306, 308 are provided, each having their own enclosure frameworks 310, 312, 314 with panelling (not shown) and each being individually isolatable and removable by means of valves (not shown), 25 as with the first embodiment. Fluorine is passed through a purification cassette comprising a duty purifier 320 and a standby purifier cassette 324 and then to a compression cassette comprising a plurality of storage tanks 326 by means of duty and standby compressors 328, 30 330. The fluorine is then piped to CVD tools, for example, for use. A supply of liquid hydrogen fluoride is held in a tank 332. A hydrogen fluoride vaporiser 334 vaporises liquid hydrogen fluoride from the tank 332 and supplies it to the cassettes 304, 306, 308 to maintain a 35 constant concentration of electrolyte. A fluorine

abatement cassette 340 is provided to remove solids from the fluorine supply, to remove fluorine from pipework when a cassette is being changed for servicing or repair, for example, and extraction of fluorine not destined for 5 customer process use. The apparatus of Figure 9 has all of the pipework purging systems, safety extraction and scrubbing systems of the first embodiment.

CLAIMS

1. Apparatus for the generation of fluorine by the electrolysis of hydrogen fluoride, the apparatus comprising: a plurality of individual fluorine generating cassettes; said individual fluorine generating cassettes being operably connected to a fluorine gas distribution system for the remote use and consumption of said fluorine gas; said fluorine generating cassettes being individually isolatable from said gas distribution system and removable from the apparatus for remote maintenance, as hereinbefore defined.
5
2. Apparatus according to claim 1 wherein the fluorine generating cassettes are connected to the apparatus by valve means for the isolation and disconnection of said fluorine generating cassettes from the apparatus.
15
3. Apparatus according to claim 2 wherein the valve means are double isolation valves have a space therebetween which space is connected to an extraction and scrubbing system.
20
4. Apparatus according to any one preceding claim wherein the fluorine generating cassettes are installed within a common apparatus main enclosure.
25
5. Apparatus according to any one preceding claim wherein all fluorine generating cassettes are substantially identical to each other.
6. Apparatus according to any one preceding claim wherein said fluorine generating cassettes are provided with wheels.
30
7. Apparatus according to any one preceding claim wherein each fluorine generating cassette is provided with an enclosure.

8. Apparatus according to claim 4 wherein said main enclosure is connected to extraction equipment and to a scrubbing system.
9. Apparatus according to claim 7 wherein each fluorine generating cassette enclosure is connected to extraction equipment and to a scrubbing system.
5
10. Apparatus according to any one preceding claim further including at least one fluorine purification cassette through which the fluorine output of said fluorine generating cassettes is passed.
10
11. Apparatus according to any one preceding claim further including at least one fluorine buffer cassette connected in the fluorine line downstream of the at least one fluorine purification cassette.
15
12. Apparatus according to claim 11 wherein the buffer cassette holds compressed fluorine.
15
13. Apparatus according to any one of preceding claims 7 to 12 wherein a fluorine generating cell within the fluorine generating cassette is fixed to said enclosure such that said enclosure provides a cathode connection to said cell.
20
14. Apparatus according to claim 13 wherein said enclosure includes a framework having panelling.
20
15. Apparatus according to either claim 13 or 14 wherein the cathode connection is at 0 volts relative to earth.
25
16. Apparatus according to any one preceding claim further including purging means to remove potentially reactive fluids from piping before fluorine is introduced thereinto.
30
17. Apparatus according to any one of preceding claims 1 to 16 wherein the apparatus is transportable as a unit by land or sea.

18. Apparatus according to claim 17 wherein the overall size of the apparatus is at most that of a standard ISO container.
19. Apparatus according to any one of preceding claims 1 to 9 wherein each of said individual fluorine generating units are further provided with a power supply unit at least for electrolysis, fluorine purification means, fluorine compression means and fluorine storage tank/buffer means.
- 10 20. A method for the operation and maintenance of apparatus for producing fluorine by the electrolysis of hydrogen fluoride, the method comprising the steps of: providing a plurality of fluorine generating cassettes operably connected to a fluorine gas distribution system for the remote use and consumption of said fluorine; providing means for isolating any individual fluorine generating cassettes from said fluorine gas distribution system and from each other; and providing means for the disconnection and removal of said isolated fluorine generating cassette from said apparatus without interruption of supply of fluorine from remaining fluorine generating cassettes.
- 15 21. A method according to claim 20 wherein the plurality of fluorine generating cassettes are provided with sufficient fluorine generating capacity such that a total demand for fluorine may be met by less than the total number of fluorine generating cassettes within said apparatus.
- 20 22. A method according to either claim 20 or claim 21 wherein an individual fluorine generating cassette may be removed from the apparatus and taken to a remote site for maintenance whilst still maintaining fluorine output to meet demand.

23. A method according to any one of preceding claims 20 to 22 further comprising the steps of providing each individual fluorine generating cassette with power supply means at least for electrolysis, fluorine purification means, fluorine compression means and fluorine storage tank/buffer means.

5

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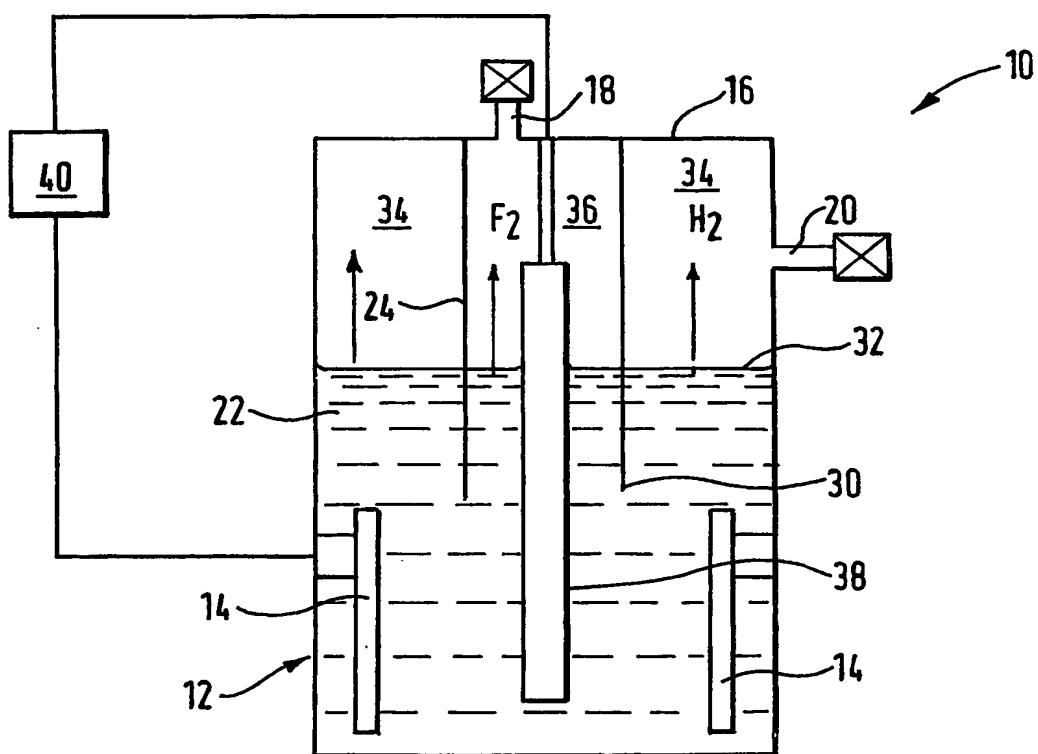


Fig.1.

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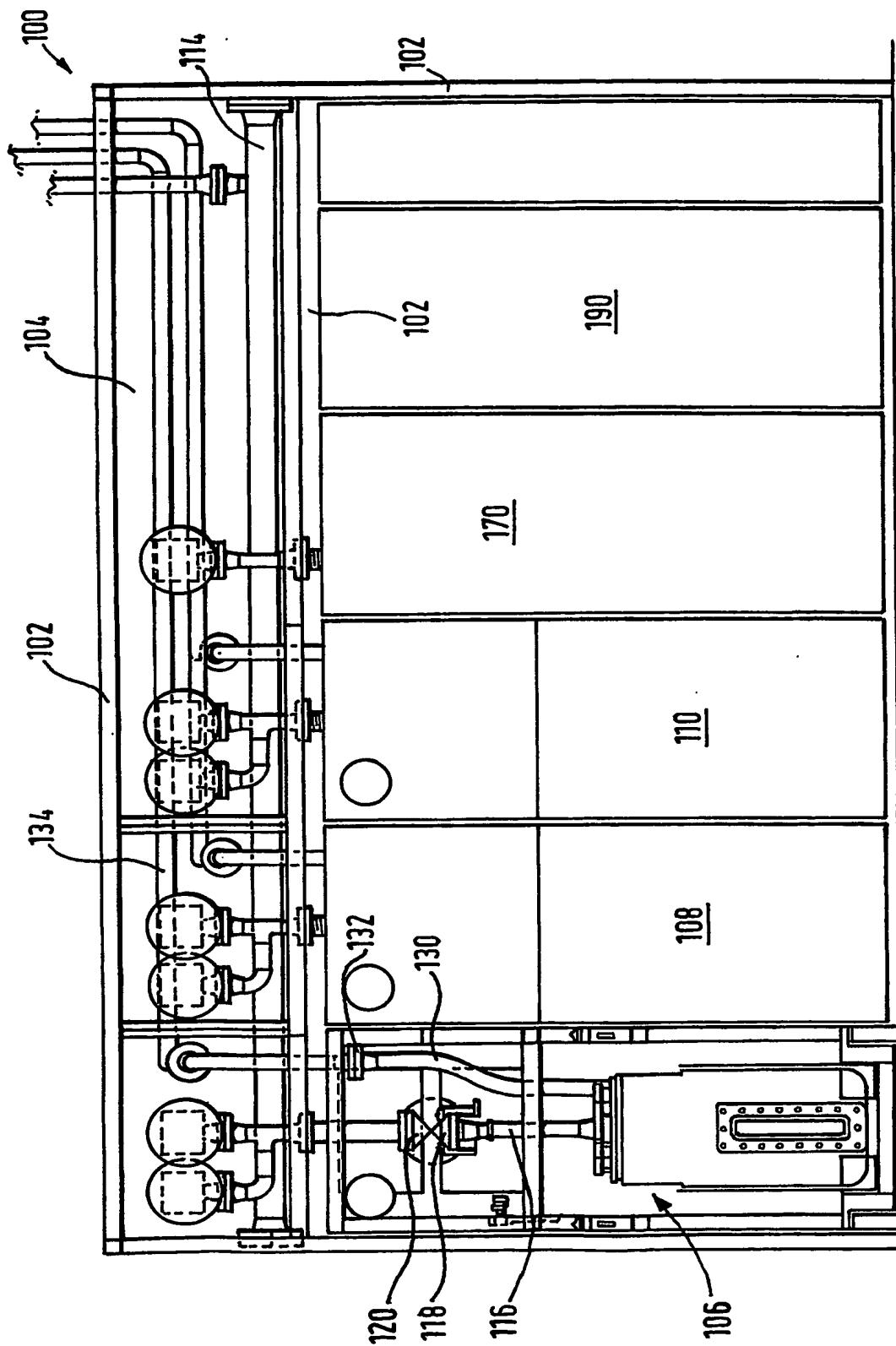


Fig. 2a.

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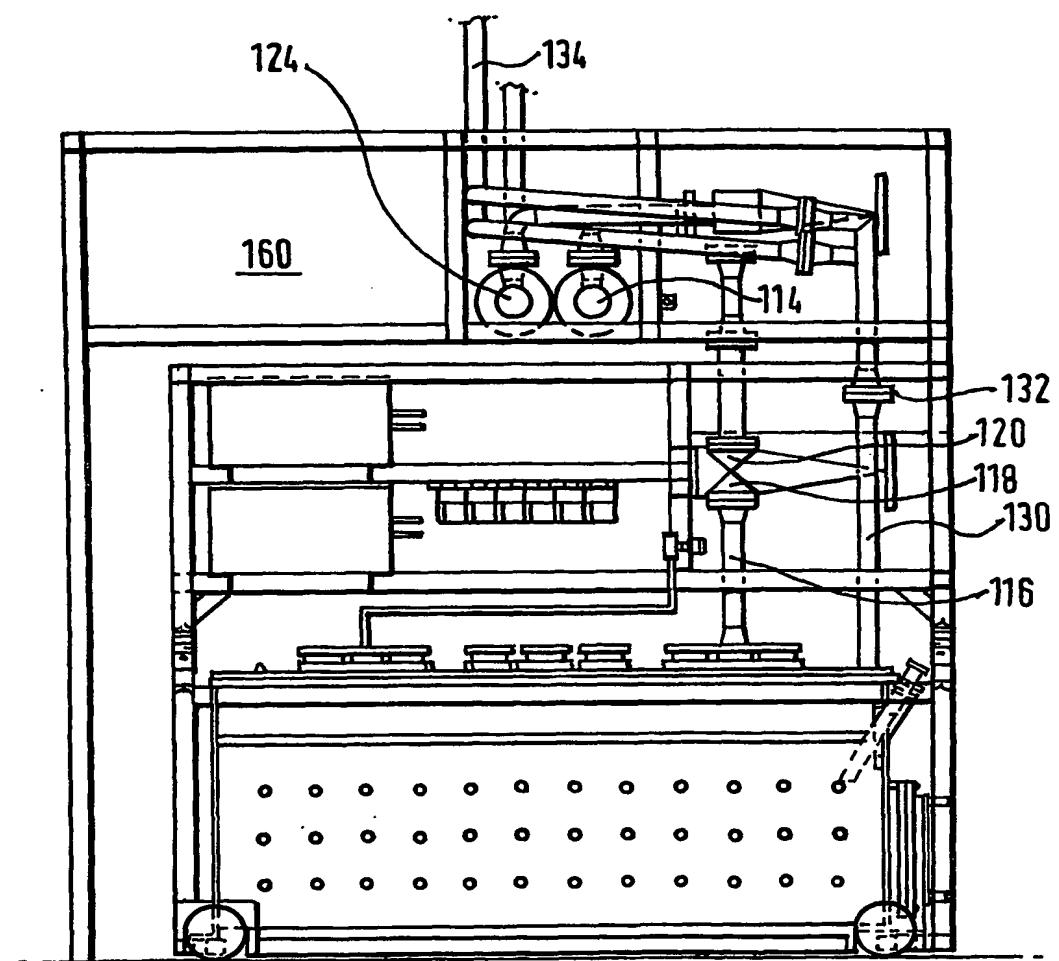
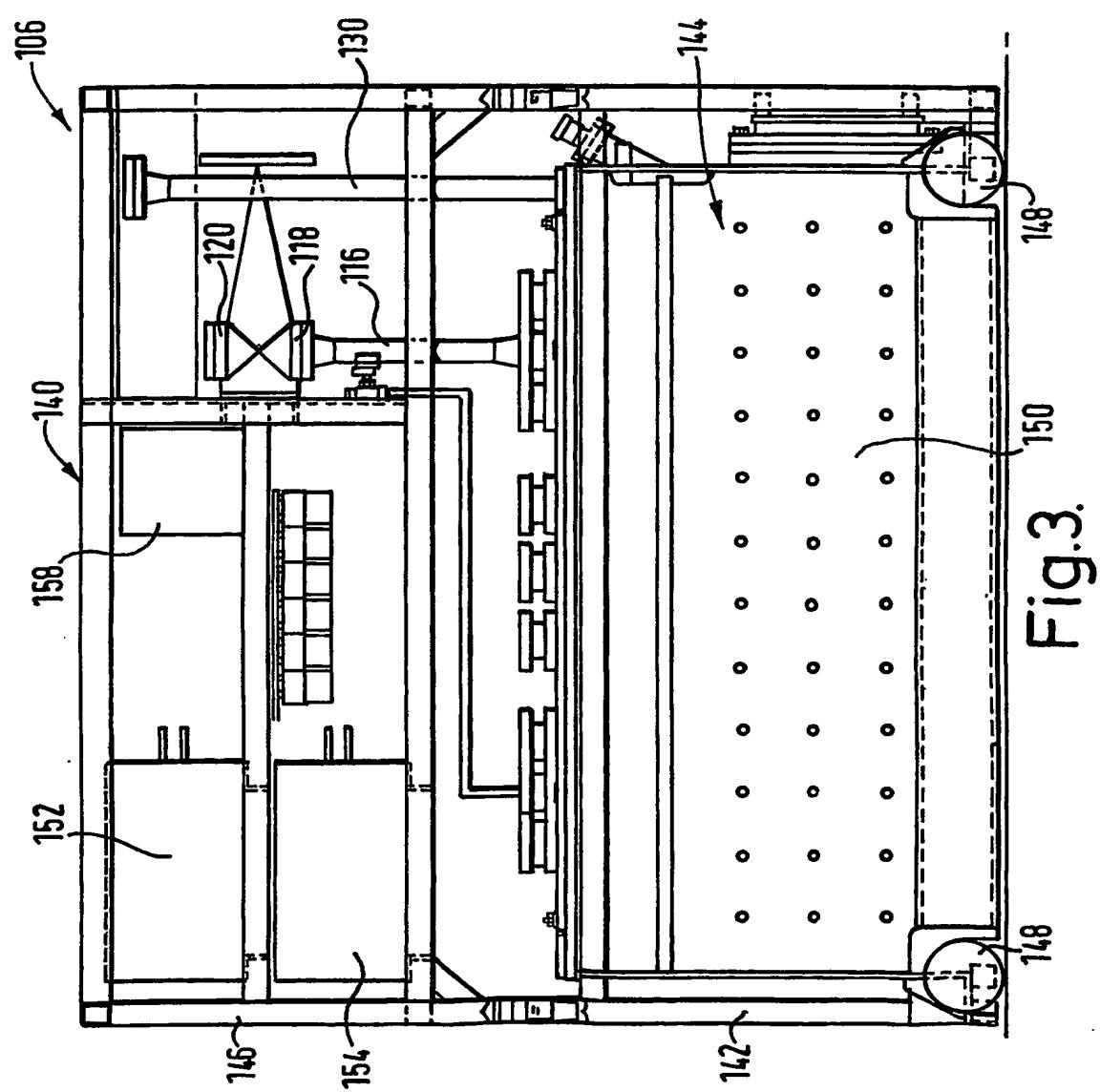
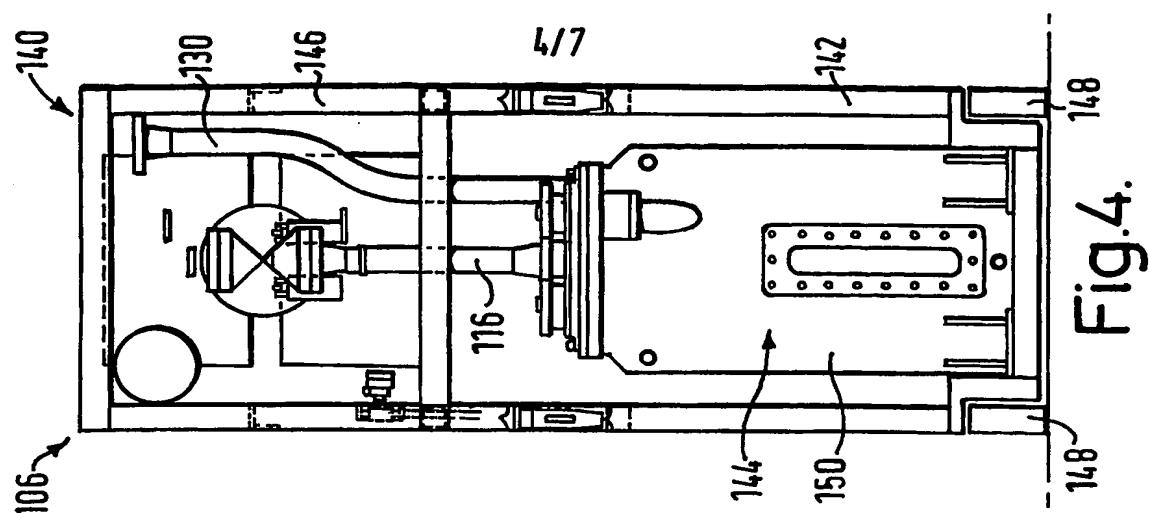


Fig.2b.



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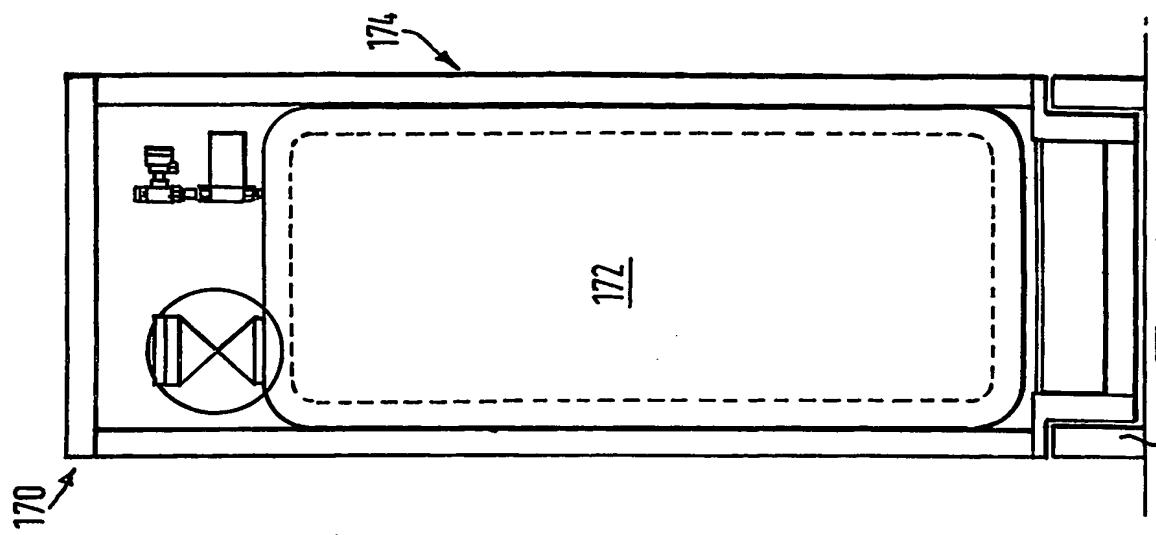


Fig.6.

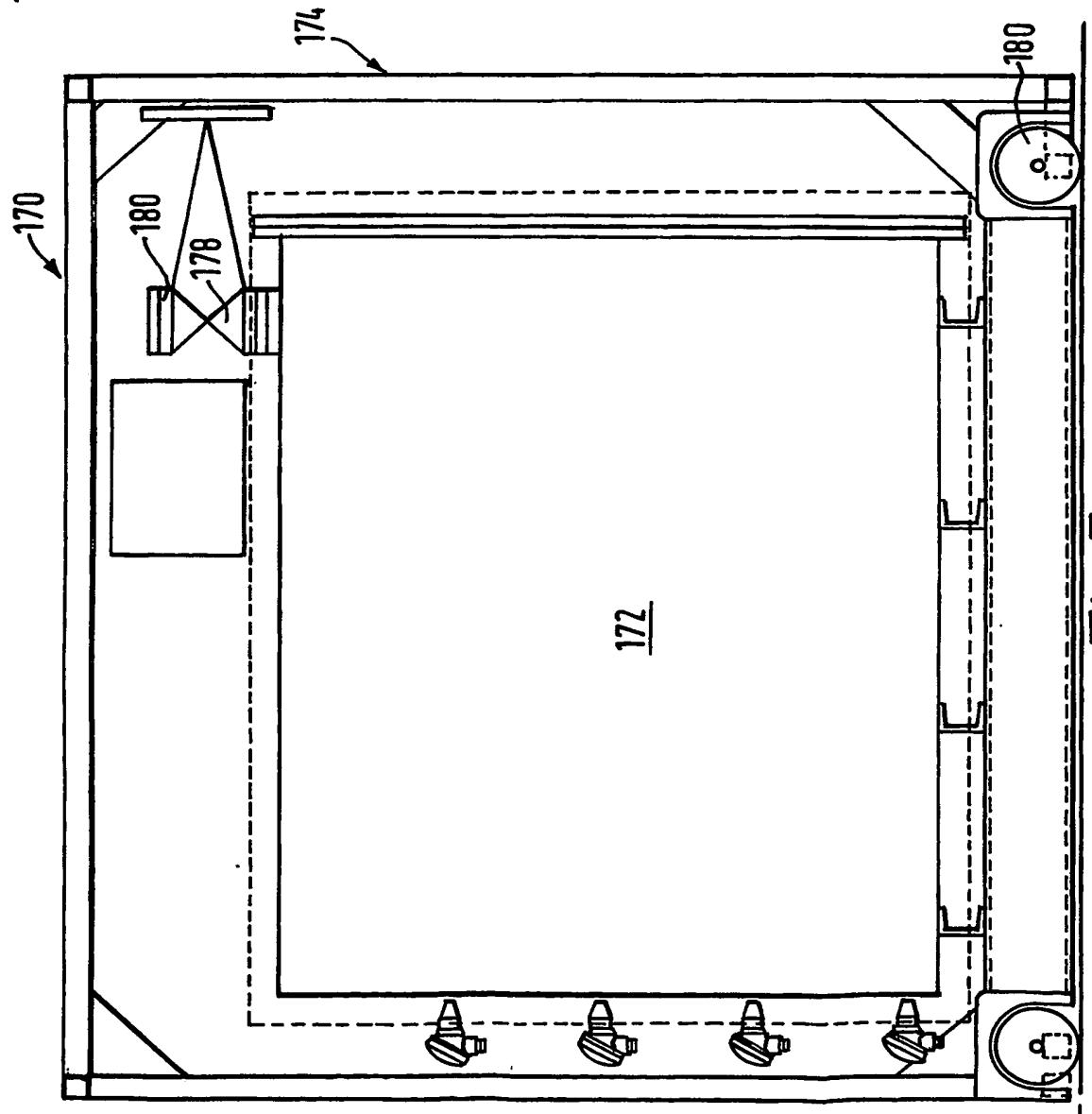
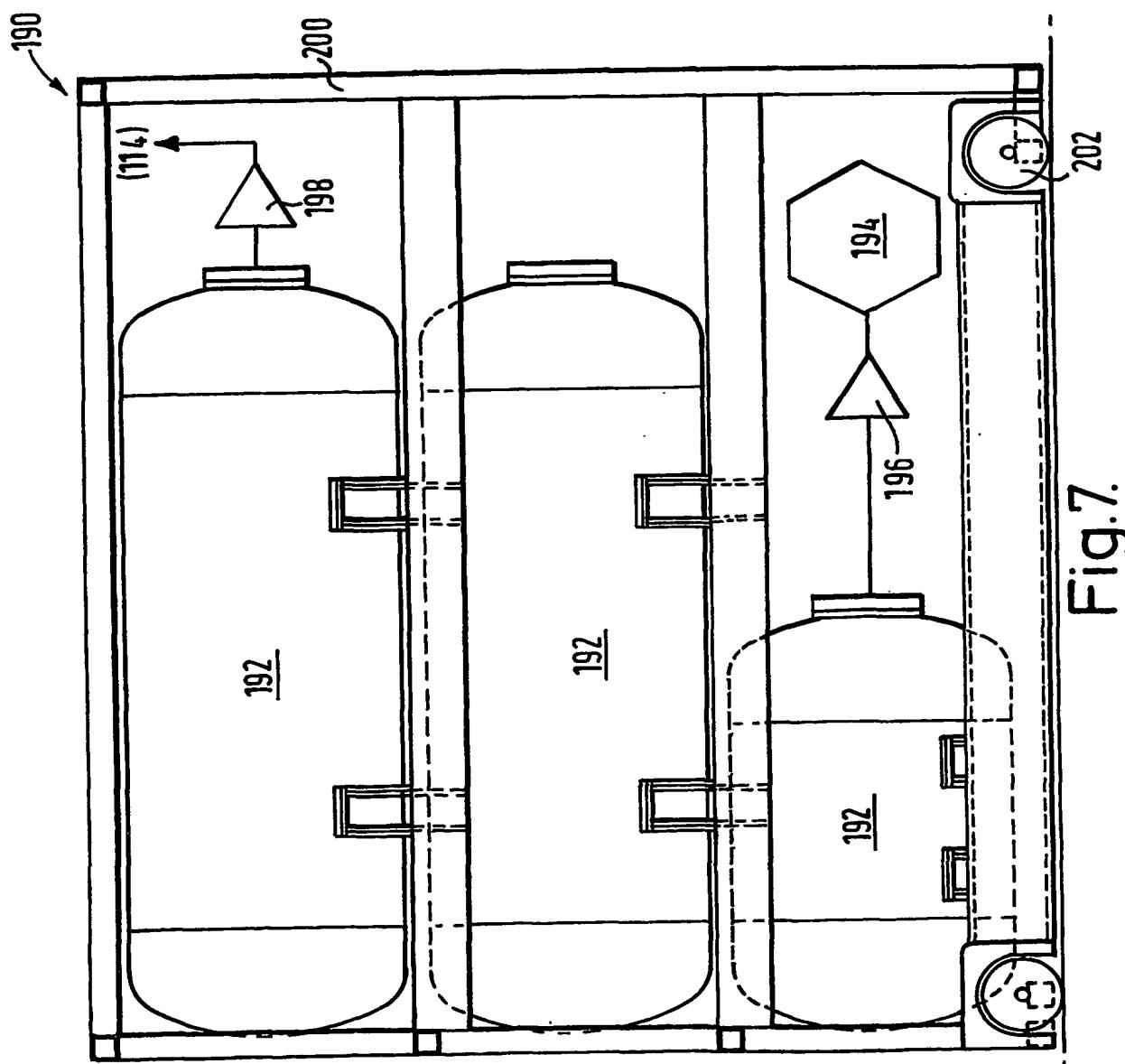
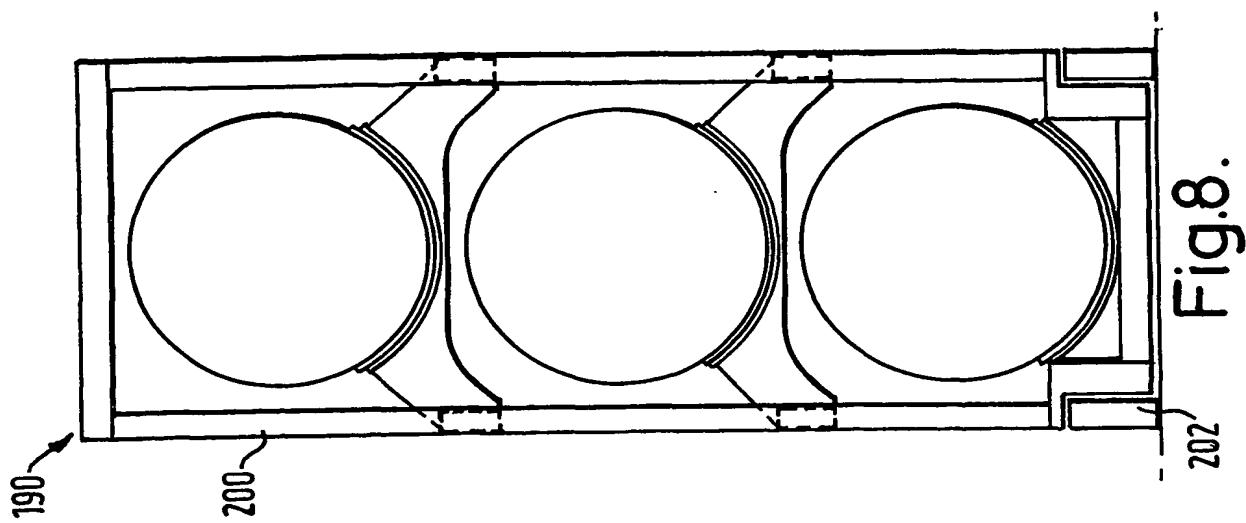


Fig.5.

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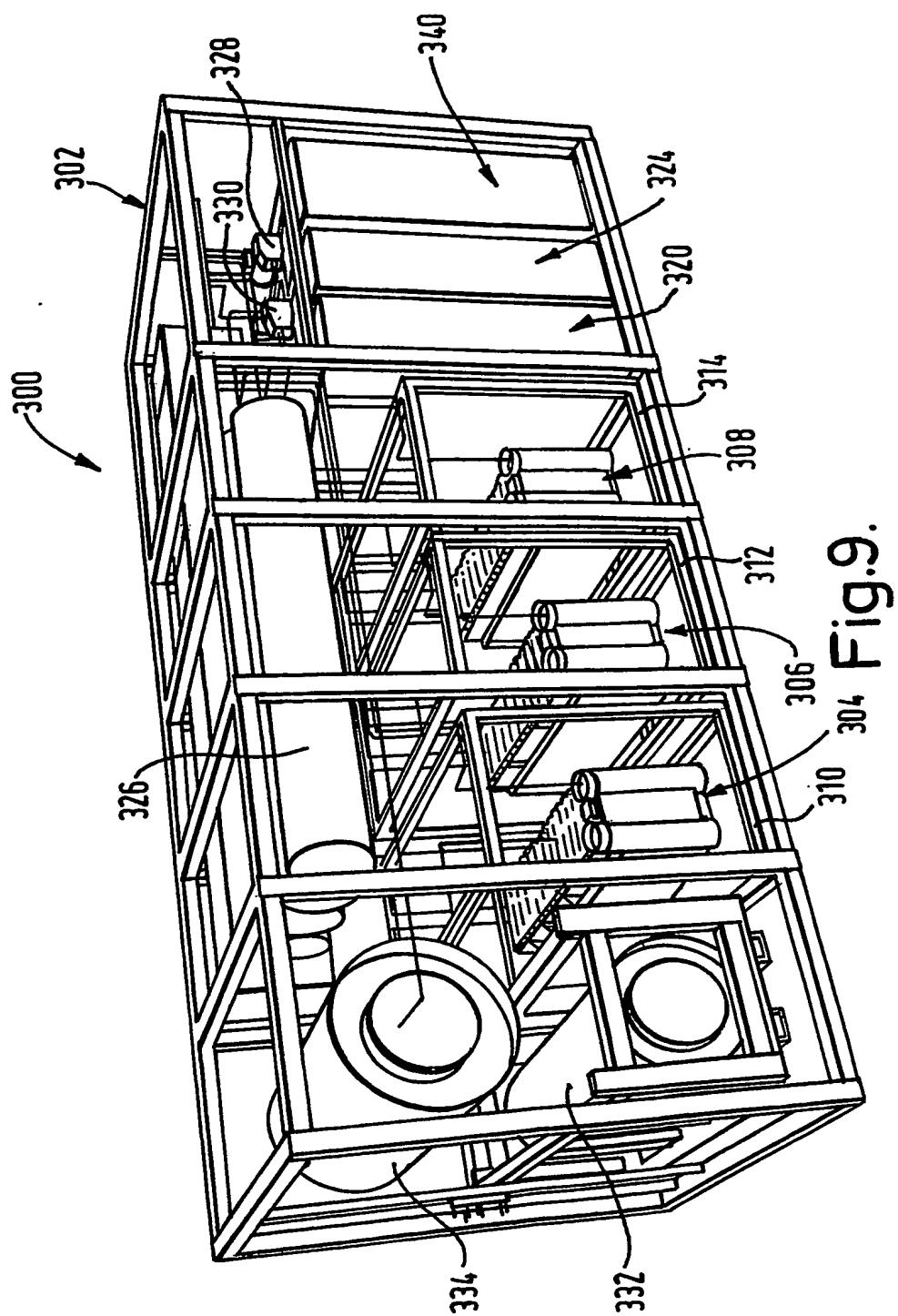


Fig. 9.
304

INTERNATIONAL SEARCH REPORT

Internat:	Application No
PCT/GB 03/03023	

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25B1/24 C25B9/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 950 370 A (TARANCON GREGORIO) 21 August 1990 (1990-08-21) column 1, line 6-10 column 2, line 56-62 column 13, line 62 -column 14, line 50 -----	1-23
A, P	EP 1 283 280 A (TOYO TANSO CO) 12 February 2003 (2003-02-12) the whole document	1-23
A	& WO 01 77412 A (TAKEBAYASHI HITOSHI; TOYO TANSO CO (JP); HIRAIWA JIRO (JP); TADA Y) 18 October 2001 (2001-10-18) -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

31 October 2003

Date of mailing of the International search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati	plication No
PCT/GB	03/03023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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